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PART II:

ENVIRONMENTAL PROTECTION AGENCY

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STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Kraft Pulp Mills

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 60]

[FRL 605-2]

KRAFT PULP MILLS

Standards of Performance for New Stationary Sources

Notice is hereby given that under the authority of section 111 of the Clean Air Act, as amended, the Administrator is proposing standards of performance for new and modified kraft pulp mills. The Administrator also is proposing to amend Appendix A, Reference Methods, in Part 60 by adding a reference method for the measurement of total reduced sulfur (TRS) emissions and an alternate method for the measurement of particulate matter.

Proposed Standards

The proposed standards would limit emissions of particulate matter from three affected facilities at kraft pulp mills. The limits are: (1) 0.10 gram per dry standard cubic meter (g/dscm) for recovery furnaces, (2) 0.15 gram per kilogram of air-dried pulp (g/kg ADP) for smelt dissolving tanks, (3) 0.15 g/dscm for lime kilns when burning natural gas, and (4) 0.30 g/dscm for lime kilns when burning oil. Visible emissions from recovery furnaces would be limited to 35 percent opacity.

Under the proposed standards, TRS emissions would be limited to 5 parts per million (ppm) by volume from seven affected facilities: Digester systems, brown stock washer systems, multiple-effect evaporator systems, black liquor oxidation systems, recovery furnaces, lime kilns, and condensate stripper systems. In addition, a TRS standard of 0.025 g/kg ADP is proposed for smelt dissolving tanks.

Environmental Impact

The proposed standards would reduce particulate emissions from new kraft pulp mills more than 99 percent below the levels that would result from no control and more than 50 percent below the average levels that are being achieved by typical existing facilities in the United States. Emissions of TRS would be reduced by more than 95 percent below the uncontrolled levels and more than 80 percent below the average levels for existing sources.

TRS emissions from kraft pulp mills are extremely odorous, and there are numerous instances of poorly controlled kraft mills creating public odor problems. The proposed standards include limitations on TRS emissions, rather than on the intensity of odors produced by kraft pulp mills, because this course of action would ensure more objective and efficient enforcement. The proposed standards would prevent odor problems from most newly constructed kraft pulp mills, except in the immediate vicinity of the mills on occasions when meteorological conditions produce downwash of stack plumes. The proposed standards would substantially reduce ground level ambient air concentrations of particulate matter around new kraft pulp mills below current levels found around existing mills.

The secondary environmental impact of the proposed standards would be minor. No additional solid waste handling or disposal problems would be caused by the standards because the additional particulate matter collected from recovery furnace systems, smelt dissolving tanks, and lime kilns can be recycled to the kraft pulping process. Increased water demand and treatment would be slight because mill process water can be used in scrubbing systems for lime kilns and smelt dissolving tanks, and the scrubbing system effluent could be recirculated to the kraft pulping process with no increased effluent. The increased mud washing necessitated by the standard could increase water demand. A relatively small amount of particulate matter, sulfur dioxide, and nitrogen oxides would be discharged into the air if the power plant that supplies the additional electrical power required by the standards is fired with fossil fuel.

Energy Impact

The energy requirements of the proposed standards have been evaluated. Compared to the requirements of the average State standards, the incremental energy that would be required to control all new, modified, and replaced affected facilities at kraft pulp mills by 1981 has been estimated at an equivalent of about 1,440,000 barrels of Number 6 fuel oil per year. The magnitude of this requirement indicates that the proposed standards would not have a major impact on the imbalance between national energy demand and domestic supply.

The incremental energy requirements of the proposed standards would be generated by the use of fans or pumps to circulate exhaust gases or scrubbing liquids through control devices, and the direct consumption of natural gas or fuel oil to incinerate exhaust gases or maintain process conditions that reduce the generation of pollutants. The incremental energy represents an increase of approximately 4.3 percent above the process energy requirements for new kraft pulp mills.

Economic Impact

The proposed regulations could affect an estimated 17 million tons of kraft pulping capacity by 1981. About a third of that capacity would be affected as a result of mill capacity expansions. The remainder would be affected via replacement of depreciated designated facilities. It is projected that the equivalent of 33 new mills or expansions at existing mills, with a capacity of 500 T ADP/day, will occur through 1980. Replacement of existing depreciated designated facilities will result at an estimated 35 mills.

Total incremental investment costs through 1981 are projected to be $104 million. The fifth-year annualized costs, including depreciation and interest, are estimated at $33 million. About a third of these costs would be incurred by mills expanding capacity, while the remainder would be incurred by mills replacing depreciated designated facilities.

The costs that new, modified, and reconstructed kraft pulp mills would incur to comply with the proposed standards are considered reasonable. No difference in impact among mill sizes could be distinguished, and the proposed standards would not have an adverse impact on either small or large mills. The capital required for typical new mills would be increased by less than 2 percent, and the price of semi-bleached kraft pulp would be increased by less than 2 percent. The effect the proposed standards would have on demand and supply of kraft pulp and on the future growth of the kraft pulp industry is considered negligible. It is emphasized that the costs are considered reasonable for new and modified sources and that it is not implied that the same costs apply to the retrofitting of existing sources. The review of the economic impact has shown that the proposal is not a major action under the Inflationary Impact Statement (IIS) program and no IIS is needed.

Selection of Source Category and Affected Facilities

Section 111 of the Act directs the Administrator to establish standards of performance for stationary sources that may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare. Kraft pulp mills are a major source of TRS compounds and particulate matter emissions. TRS compounds can have an adverse effect on public welfare, and particulate matter can have an adverse effect on public health and welfare. Kraft pulp mills were selected for the development of standards based on expected growth of the industry and the beneficial impact that would result from the application of best technology for air pollution control. Kraft pulping has historically been a rapidly growing industry, with a growth rate of 5.5 percent per year between 1956 and 1975. The annual growth rate for 1976 to 1978 is projected to be 2.5 percent, but estimates show that the growth rate may return to a higher rate in 1979.

TRS emissions from kraft pulp mills are composed primarily of hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. These sulfide compounds are extremely odorous and exhibit odor threshold concentrations of no more than a few parts per billion. A study of the national social and economic impacts of odors performed in 1971–1973 by Copley International Corporation for EPA found that the pulp and paper industry ranks in the upper quarter of all odor sources in terms of strength and public objection to the odors. The emissions from each pulp mill surveyed in the study affect an average of 44,000 persons over an area of approximately 100 square miles. The survey of 184 local air pollution control agencies in the United States ranked the pulp and paper source category as the fastest growing odor problem.

The establishment of standards of performance for TRS emissions from kraft pulp mills under section 111 of the Act would involve section 111(d) which provides for control of any air pollutants which are not on lists published pursuant to section 108(a) or 112(b)(1)(A) of the Act. TRS has not been named on either list. Specifically, section 111(d) requires that the Administrator prescribe a procedure to assure that States develop, implement, and enforce emission standards for existing sources that would be subject to the standard of performance if they were new sources. EPA promulgated regulations that establish procedures and requirements for submittal of State plans under section 111(d) on November 17, 1975 (40 FR 53339). As a consequence of the provisions of section 111(d), promulgation of this standard of performance for new and modified sources would require that the States develop emission standards for existing kraft pulp mills.

The proposed standards would apply to all process gas streams which have been identified as major sources of TRS compounds or particulate matter at kraft pulp mills. The following affected facilities are specified by the proposed standards: (1) Digester system, (2) brown stock washer system, (3) multiple-effect evaporator system, (4) black liquor oxidation system, (5) recovery furnace, (6) smelt dissolving tank, (7) lime kiln, and (8) condensate stripping system.

Water treatment ponds are significant sources of TRS emissions at some kraft pulp mills. Evaluations of odors in the immediate vicinity of mills indicate that TRS emissions from these ponds vary considerably from source to source, and do not produce an odor problem at some mills. Methods for measuring TRS emissions from kraft pulp mill water treatment ponds are not available at this time, and the proposed standards would not apply to these facilities. Emissions from ponds can be avoided by treating the process condensate stream in a condensate stripper system prior to discharge into the pond, but bacterial action could generate additional TRS in some ponds. EPA intends to further investigate measurement and emission control methods for water treatment ponds at kraft pulp mills, and determine whether regulation under the performance standard is appropriate.

Bark and power boilers are two sources of particulate emissions at kraft pulp mills that are not covered by the proposed standards. EPA plans to develop new source performance standards for industrial boilers, and this source category will include boilers at kraft pulp mills.

Rationale

The bases for the proposed standards include include information derived from (1) available technical literature on the kraft pulping industry and emission control of the kraft pulping process, (2) published studies sponsored by EPA of emission control of the kraft pulping process, (3) information gathered during visits to pollution control agencies and kraft pulp mills in the United States, (4) comments and suggestions solicited from experts, and (5) the results of measurements of emissions conducted by EPA and by the industry. The proposed standards for TRS emissions would require combinations of several control methods:

1. Use of improved process operating procedures to reduce the generation of TRS, such as control of the black liquor firing rate, the oxygen concentration within the furnace, and the air-to-solids ratio during operation (recovery furnace); more efficient mud washing and control of temperature and oxygen concentration (lime kiln); and use of clean water that is low in dissolved sulfides in the particulate scrubber (smelt dissolving tank).

2. Use of process equipment such as the indirect-contact evaporator system or black liquor oxidation system that inherently reduces the generation of TRS (recovery furnance system).

3. Use of control equipment such as scrubbers with caustic solution to collect TRS (lime kiln).

4. Use of incineration to convert TRS into less objectionable compounds (digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, and condensate stripper system).

Recovery Furnace

The recovery furnace is the largest single source of particulate matter and TRS at a kraft pulp mill. In the direct-contact conventional furnace, heat is recovered by directly contacting the furnace combustion gases with black liquor in a direct-contact evaporator. Most of the TRS discharged from direct-contact recovery furnaces is generated in the direct-contact evaporator, which also collects an appreciable portion of the particulate matter generated by the combustion of black liquor in the furnace.

The two methods for reducing TRS emissions from recovery furnaces are: (1) The use of a black liquor oxidation system to reduce the sodium sulfide content of the black liquor before evaporation in a direct-contact evaporator, and thereby the formation of TRS in the direct-contact evaporator, and (2) the elimination of the direct-contact evaporator in an indirect-contact recovery furnace. Since comparable emission levels of TRS can be achieved by these two control methods, the proposed standards could be attained by using either type of recovery furnace. However, the proposed emission limit of 5 ppm TRS, four-hour average, is lower than that being achieved by some existing recovery furnaces of either type and would therefore require more careful operation and additional black liquor oxidation for comparable new furnaces.

Electrostatic precipitators (ESP's) are used almost universally to control particulate matter emissions from kraft recovery furnaces. Scrubbers with relatively low collection efficiencies are in use at a few facilities. Tests performed by EPA demonstrate that the proposed particulate standard could be achieved by a properly designed and well maintained ESP.

The industry has stated that ESP's operated on kraft recovery furnaces significantly deteriorate over the life of the ESP even when it is well maintained. In response, EPA obtained information from mill operators and vendors of ESP's and concluded that good maintenance of wires, collection plates, and rapping systems would ensure that particulate matter emissions from a properly designed and operated ESP would not increase to a large extent over the life of the ESP. EPA recognizes that ESP's for kraft recovery furnaces must withstand more severe service than for some other applications. Accordingly, the proposed standards would require the more ruggedly designed ESP's in order to accommodate, for example, the more severe plate rapping and stressing of wires experienced at kraft pulp mills. The additional cost of the more ruggedly designed ESP was included in the economic analysis and is considered to be reasonable.

The industry has also stated that the performance of ESP's operated on kraft recovery furnaces should be allowed to deteriorate until there is a sufficient amount of maintenance to be performed that the necessary shutdown of the furnace would be justified. EPA believes that this is a reasonable approach. Accordingly, the proposed particulate matter standard for recovery furnaces would allow some deterioration; the proposed emission limit has been set somewhat higher than the levels known to be achievable on the basis of both the results of particulate matter tests performed by EPA and design levels for new kraft recovery furnace ESP's.

EPA has determined that an oxygen concentration in excess of 8 percent in the gas stream measured after the recovery furnace control device represents excessive air inleakage and results in excessive dilution of the gas stream. The proposed standard, therefore, requires that all concentrations of particulate matter and TRS measured after the recovery furnace control device that have an oxygen concentration in excess of 8 percent be corrected to 8 percent oxygen.

Lime Kiln

Lime kilns are a major source of particulate matter emissions at kraft pulp mills. Because the lime mud that is processed in the kiln contains residual quantities of sulfides, lime kilns are also sources of TRS emissions.

The two methods for controlling TRS emissions from lime kilns are: (1) more efficient washing to reduce the sulfide content of the lime mud, and control of kiln exhaust gas temperature and oxygen content, and (2) use of sodium hydroxide (caustic) in the scrubber that controls particulate emissions from most kilns. Tests carried out by EPA demonstrate that when the first TRS control method (process control) is applied, the simultaneous addition of caustic to a scrubber produces a significant reduction in TRS emissions below that achievable with

process control alone. The annualized cost for caustic addition to the scrubber is small where the caustic is not part of the make-up in the kraft causticizing system. Accordingly, the proposed standard of 5 ppm TRS, four-hour average, would require both the best process controls for lime kiln operation and caustic addition to the scrubber, or an equivalent system.

In developing the proposed standards, EPA carried out six tests for particulate emissions from lime kilns. In each case the control device for particulate matter was a medium pressure drop scrubber, the most widely used control technique in the domestic industry. However, one domestic kraft pulp mill controls particulate emissions with an electrostatic precipitator. Based on design parameters and emission data supplied by the operator of this ESP, this system achieves an emission level significantly below that determined by EPA for medium pressure drop scrubbers. However, the waste gases from the digester system and multiple-effect evaporator system, which could more economically be incinerated in the lime kiln, are processed in a separate incinerator at this facility to control TRS emissions. The cost and energy penalties for the separate incinerator are relatively large. The industry has commented that it may not be feasible to incinerate the waste gases from other sources in a kiln controlled by an ESP, because gases may explode in the ESP when flameouts occur in the kiln. Solutions to this potential problem, such as automatic diverting of inlet gases away from the kiln when a flameout occurs, have been considered, but there is at this time no demonstrated technology that will ensure that explosions would not occur.

In arriving at the proposed standard for particulate matter emissions from lime kilns, EPA considered the alternatives of a medium pressure drop scrubber alone, an ESP alone, and both particulate control systems operated in series. A separate incinerator to control TRS emissions from digester systems, multiple-effect evaporator systems, and condensate stripper systems was included in the two alternative ESP systems. EPA concluded that the relatively large increments in cost and energy usage associated with the ESP alternatives were not justified by the additional particulate control gained beyond that achievable with a medium pressure drop scrubber alone. Consequently, the proposed particulate matter standard would require a medium pressure drop scrubber (approximately 30 inches water gauge), or equivalent.

EPA has determined that an oxygen concentration in the gas stream measured after the lime kiln control device in excess of 10 percent represents excessive air inleakage; therefore, the proposed standards require that all measurements of particulate matter and TRS that have an oxygen concentration in excess of 10 percent be corrected to 10 percent oxygen.

Smelt Dissolving Tank

Smelt dissolving tanks discharge particulate matter comprised of finely divided smelt particles that are entrained in the steam emitted from the tank. On an uncontrolled basis, the quantity of particulate emissions is small in comparison with that from recovery furnaces and lime kilns. TRS emissions can be generated in the dissolving tank or in a scrubbing device that collects particulate matter, depending primarily on the sulfide content of water used to dissolve the smelt and to perform the scrubbing. Standards in terms of concentration of pollutants are not considered appropriate for smelt dissolving tanks because the effluent stream is primarily air and no correction for oxygen content and dilution air is possible to ensure effective enforcement.

Particulate emissions from smelt dissolving tanks are controlled by using wire mesh demister pads or low energy scrubbers. The scrubbers remove particulate matter much more effectively, though the energy requirements and operating costs are higher than for demisters. The proposed particulate standard for smelt dissolving tanks would require the use of low energy scrubbers, or equivalent systems, and is supported by four EPA tests on two types of low energy scrubbers. The proposed TRS standard for smelt dissolving tanks would prevent the use of water highly contaminated with sulfides for dissolving the smelt and for particulate scrubbing systems.

Other Sources

Approximately one-quarter of the total uncontrolled TRS emissions from a typical kraft pulp mill are generated by the digester system, brown stock washer system, black liquor oxidation system, multiple-effect evaporator system, and condensate stripper system. Ineffective control of these facilities could have a large impact on localized odor problems. The effluent streams can be incinerated in the recovery furnace, the lime kiln, or a separate incinerator to oxidize most of the TRS. The quantity of auxiliary fuel required for incineration is greatly reduced if incineration is performed in the recovery furnace and the lime kiln. If the noncondensable gases from the brown stock washer system and the black liquor oxidation system are incinerated, for example, in the recovery furnace, some auxiliary fuel may be required. However, the noncondensable gases from the digester system, multiple-effect evaporator system, and condensate stripper system would not require additional fuel if incinerated in the lime kiln as part of the primary air feed to the kiln. The proposed standard of 5 ppm TRS, four-hour average, for each of these five affected facilities would require incineration in the recovery furnace and the lime kiln, or equivalent.

Opacity Standard

An opacity standard is proposed for recovery furnace systems to ensure proper operation and maintenance of the particulate control device. No opacity standards are proposed for lime kilns and smelt dissolving tanks, which frequently generate persistent plumes of condensed water vapor. The effluent plume is so greatly dispersed by the time the vapor plume disappears that the observed opacity would not be as effective an indicator of the performance of the patriculate control system as other parameters. Monitoring the operating parameters of the control system would be more effective.

State Implementation Plans

It should be noted that standards of performance for new sources established under section 111 of the Clean Air Act reflect emission limits achievable with the best adequately demonstrated systems of emission reduction considering the cost of such systems. State implementation plans (SIP's) approved or promulgated under section 110 of the Act, on the other hand, must provide for the attainment and maintenance of national ambient air quality standards (NAAQS) designed to protect public health and welfare. For that purpose SIP's must in some cases require greater emission reductions than those required by standards of performance for new sources. In addition, States are free under section 116 of the Act to establish more stringent emission limits than those established under section 111 or those necessary to attain or maintain the NAAQS under section 110. Thus, new and existing sources may in some cases be subject to limitations more stringent than EPA's standards of performance under section 111.

Testing, Monitoring, and Recordkeeping

Under the proposed standards, performance tests for TRS emissions according to Reference Method 16 proposed herein would be required for all affected facilities. Performance tests for particulate matter emissions from recovery furnace systems, lime kilns, and smelt dissolving tanks would also be required. Particulate matter emissions would be measured by Reference Methods 1 through 5. Method 17 (in-stack filter) is being proposed as an alternative method to measure particulate emissions from the recovery furnace. It is being proposed in Appendix A, Reference Methods, because the Agency intends to also propose Method 17 as a reference method to measure particulate matter from grain elevators.

The proposed standards include provisions for continuously monitoring the opacity of visible emissions discharged from recovery furnaces. To ensure proper operation and maintenance of scrubbers installed on lime kilns and on smelt dissolving tanks, provisions are included for monitoring the pressure drop across the scrubber and the scrubbing fluid supply pressure to the scrubber.

Where emissions from the digester system, brown stock washer system,

multiple-effect evaporator system, black liquor oxidation system, or condensate stripper are incinerated in a device other than a lime kiln or recovery furnace, it is proposed that the firebox temperature of the device be monitored.

A requirement for the continuous monitoring of TRS emissions from the recovery furnace and lime kiln is also proposed. The specifications for continuous TRS monitors are not being proposed at this time because they have not been completely developed. However, the development of these specifications are imminent and they are expected to be promulgated at the time that the kraft pulp mill standards of performance are promulgated.

A requirement to monitor the oxygen concentration of the gas stream on a dry basis after the control device is being proposed for the lime kiln and recovery furnace. The montoring of oxygen concentrations is necessary to correct the TRS and particulate concentrations for the lime kiln and recovery furnace when the oxygen concentrations in the respective gas streams are in excess of 10 percent and 8 percent oxygen.

Records of performance testing measurements, continuous monitoring system measurements, and monitoring device measurement would have to be retained for at least two years following the date of the measurements by owners or operators subject to the provisions of this subpart. This requirement is included under § 60.7(d) of the regulation.

PUBLIC PARTICIPATION

As prescribed by section 111, this proposal of standards of performance has been preceded by the Administrator's determination that kraft pulp mills contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare and by his publication of this determination in this issue of the FEDERAL REGISTER. In accordance with section 117 of the Act, publication of these proposed standards was preceded by consultation with appropriate advisory committees, independent experts, and Federal departments and agencies.

Interested persons may participate in this rulemaking by submitting written comments (in triplicate) to the Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, Attention: Mr. Don R. Goodwin. The Administrator will welcome comments on all aspects of the proposed regulations, including the designation of kraft pulp mills as a significant contributor to air pollution which causes or contributes to the endangerment of public health or welfare, economic and technological issues, and the proposed test methods. All relevant comments received on or before November 22, 1976 will be considered. Comments received will be available for public inspection and copying at the EPA Public Information Reference Unit, Room 2922 (EPA Library), 401 M Street, S.W., Washington, D.C. 20460.

Background information on these proposed standards of performance has been published in a document entitled "Standards Support and Environmental Impact Statement: Standards of Performance for Kraft Pulp Mills, Volume 1." This report presents the factors considered in the development of the proposed standards, including alternative emission control systems, emission test data, environmental impact, costs, and economic considerations. Copies of the document may be obtained free of charge by writing to the Public Information Center (PM-215), U.S. Environmental Protection Agency, Washington, D.C. 20460 (specify "Standards Support and Environmental Impact Statement: Standards of Performance for Kraft Pulp Mills, Volume 1").

AUTHORITY: This notice of proposed rulemaking is issued under the authority of secs. 111, 114, and 301(a) of the Clean Air Act, as amended (42 U.S.C. 1857c-6, 1857c-9, 1857g(a)).

Dated: September 16, 1976.

JOHN QUARLES,
Acting Administrator.

It is proposed to amend Part 60 of Chapter I of Title 40 of the Code of Federal Regulations as follows:

1. By adding subpart BB as follows:

Subpart BB—Standards of Performance for Kraft Pulp Mills

Sec.

60.280 Applicability and designation of affected facility.
60.281 Definitions.
60.282 Standard for particulate matter.
60.283 Standard for total reduced sulfur (TRS).
60.284 Monitoring of emissions and operations.
60.285 Test methods and procedures.

AUTHORITY: Secs. 111, 114, and 301(a) of the Clean Air Act, as amended by sec. 4(a) of Pub. L. 91-604, 84 Stat. 1678 and by sec. 15 (c) (2) of Pub. L. 91-604, 84 Stat. 1713 (42 U.S.C. 1857c-6, 1857c-9, and 1857g(a)).

Subpart BB—Standards of Performance for Kraft Pulp Mills

§ 60.280 Applicability and designation of affected facility.

The provisions of this subpart are applicable to the following affected facilities in kraft pulp mills: digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, recovery furnace, smelt dissolving tank, lime kiln, and condensate stripper system. In pulp mills in which kraft pulping is combined with neutral sulfide semichemical pulping, the provisions of this subpart are applicable when any portion of the material charged to an affected facility is produced by the kraft pulping operation.

§ 60.281 Definitions.

As used in this subpart, all terms not defined herein shall have the same meaning given them in the Act and in Subpart A.

(a) "Kraft pulp mill" means any stationary source which produces pulp from wood by cooking (digesting) wood chips in a water solution of sodium hydroxide and sodium sulfide (white liquor) at high temperature and pressure. Regeneration of the cooking chemicals through a recovery process is also considered part of the kraft pulp mill.

(b) "Neutral sulfite semichemical pulping operation" means any operation in which pulp is produced from wood by cooking (digesting) wood chips in a solution of sodium sulfite and sodium bicarbonate, followed by mechanical defibrating (grinding).

(c) "Total reduced sulfur (TRS)" means the sum of the sulfur compounds, primarily hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide, that are released during the kraft pulping operation and measured by Method 16.

(d) "Digester system" means each continuous digester or each batch digester used for the cooking of wood in white liquor, and associated flash tank(s), blow tank(s), chip steamer(s), and condenser(s).

(e) "Brown stock washer system" means knotters, vacuum pumps, and filtrate tanks used to wash the pulp following the digester system.

(f) "Multiple-effect evaporator system" means the multiple-effect evaporators and associated condenser(s) and hotwell(s) used to concentrate the spent cooking liquid that is separated from the pulp (black liquor).

(g) "Black liquor oxidation system" means the vessels used to oxidize, with air or oxygen, the black liquor, and associated storage tank(s).

(h) "Recovery furnace" means the unit used for burning black liquor to recover chemicals consisting primarily of sodium carbonate and sodium sulfide. The recovery furnance includes the direct-contact evaporator for a conventional furnace.

(i) "Smelt dissolving tank" means a vessel used for dissolving the smelt collected from the recovery furnace.

(j) "Lime kiln" means a unit used to calcine lime mud, which consists primarily of calcium carbonate, into quicklime, which is calcium oxide.

(k) "Condensate stripper system" means a column, and associated condensers, used to strip, with air or steam, TRS compounds from condensate streams from various processes within a kraft pulp mill.

§ 60.282 Standard for particulate matter.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere:

(1) From any recovery furnace any gases which:

(i) Contain particulate matter in excess of 0.10 g/dscm (0.044 gr/dscf).

(ii) Exhibit 35 percent opacity or greater.

(2) From any smelt dissolving tank any gases which contain particulate matter in excess of 0.15 g/Kg ADP (0.3 lb/ton ADP).

(3) From any lime kiln any gases which:

(i) Contain particulate matter in excess of 0.15 g/dscm (0.067 gr/dscf) when gaseous fossil fuel is burned.

(ii) Contain particulate matter in excess of 0.30 g/dscm (0.13 gr/dscf) when liquid fossil fuel is burned.

§ 60.283 Standard for total reduced sulfur (TRS).

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere:

(1) From any digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, or condensate stripper system any gases which contain TRS in excess of 5 parts per million (ppm) by volume, except as provided under paragraph (b) of this section.

(2) From any recovery furnace any gases which contain TRS in excess of 5 ppm by volume.

(3) From any smelt dissolving tank any gases which contain TRS in excess of 0.025 g/Kg ADP (0.0125 lb/ton ADP).

(4) From any lime kiln any gases which contain TRS in excess of 5 ppm by volume.

(b) The Administrator may exempt any new, modified, or reconstructed black liquor oxidation system or brown stock washer system at an existing kraft pulp mill provided the owner or operator demonstrates that incinerating the exhaust gases from such system in an existing recovery furnace is technologically and economically not feasible. Any exempt system will become subject to the provisions of this subpart if the recovery furnace is changed so that the gases can be incinerated.

§ 60.284 Monitoring of emissions and operations.

(a) Any owner or operator subject to the provisions of this subpart shall install, calibrate, maintain, and operate the following continuous monitoring systems:

(1) A continuous monitoring system to monitor and record the opacity of the gases discharged into the atmosphere from any recovery furnace. The span of this system shall be set at 50 percent opacity.

(2) A continuous monitoring system, except as provided in paragraph (b)(1) of this section, to monitor and record the concentration of TRS emissions discharged into the atmosphere from any digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, recovery furnace, lime kiln, or condensate stripper system. The span shall be set at a TRS concentration of 30 ppm.

(3) A continuous monitoring system to monitor and record the percent of oxygen by volume in the gases discharged from any recovery furnace or lime kiln. The continuous monitoring system shall be located downstream of the control device(s) for the recovery furnace or lime kiln, and all measurements shall be made on a dry basis. The span of this system shall be set at 20 percent oxygen.

(b) Any owner or operator subject to the provisions of this subpart shall install, calibrate, maintain, and operate the following continuous monitoring devices:

(1) A monitoring device which measures the combustion temperature at the point of incineration of effluent gases which are emitted from any digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, or condensate stripper system and which are combusted in a power boiler or separate incineration unit. The monitoring device is to be certified by the manufacturer to be accurate within ±2° C (±3.6° F).

(2) For any lime kiln or smelt dissolving tank using a scrubber emission control device:

(i) A monitoring device for the continuous measurement of the pressure loss of the gas stream through the control equipment. The monitoring device is to be certified by the manufacturer to be accurate to within a gage pressure of ±250 pascals (ca. ±1 inch water gage pressure).

(ii) A monitoring device for the continuous measurement of the scrubbing liquid supply pressure to the control equipment. The monitoring device is to be certified by the manufacturer to be accurate within ±5 percent of design scrubbing liquid supply pressure. The pressure sensor or tap is to be located close to the scrubber liquid discharge point. The Administrator may be consulted for approval of alternative locations.

(c) Any owner or operator subject to the provisions of this subpart shall calculate and record on a daily basis:

(1) Four-hour average TRS concentrations for the six consecutive four-hour periods of each operating day. Each four-hour average shall be determined as the arithmetic mean of the appropriate four contiguous one-hour average total reduced sulfur concentrations provided by each continuous monitoring system installed under paragraph (a)(2) of this section.

(2) Four-hour average oxygen concentrations for the six consecutive four-hour periods of each operating day for the recovery furnace and lime kiln. These four-hour averages shall correspond to the four-hour average TRS concentrations under paragraph (c)(1) of this section and shall be determined as an arithmetic mean of the appropriate four contiguous one-hour average oxygen concentrations provided by each continuous monitoring system installed under paragraph (a)(3) of this section.

(d) Any owner or operator of a recovery furnace or lime kiln subject to the provisions of this subpart shall:

(1) Correct any four-hour average TRS concentration corresponding to a four-hour average oxygen concentration that is in excess of 8 volume percent for the recovery furnace. The concentration shall be corrected to 8 volume percent oxygen.

(2) Correct any four-hour average TRS concentration corresponding to a four-hour average oxygen concentration that is in excess of 10 volume percent for the lime kiln. The concentration shall be corrected to 10 volume percent oxygen.

(3) Calculate the corrections required in paragraphs (d)(1) and (2) of this section according to the following equation:

$$C_{corr} = C_{meas} \times \left(\frac{21-X}{21-Y}\right)$$

where:

C_{corr} = the four-hour TRS concentration corrected for oxygen.

C_{meas} = the four-hour average measured TRS concentration uncorrected for oxygen.

X = the volumetric oxygen concentration in percentage to be corrected to (8 percent for the recovery furnace and 10 percent for the lime kiln).

Y = the measured four-hour average volumetric oxygen concentration above 8 volume percent for the recovery furnance and above 10 volume percent for the lime kilm.

(e) For the purpose of reports required under § 60.7(c), any owner or operator subject to the provisions of this subpart shall report periods of excess emissions as follows:

(1) For emissions from the recovery furnace:

(i) All four-hour averages of TRS concentrations above 5 ppm.

(ii) All six-minute average opacities that exceed 35 percent, except that 5 percent of the averages may exceed 35 percent opacity. The exception does not apply to excess emissions due to malfunctions, startups, or shutdowns of the facility or control device.

(2) For emissions from the lime kiln: All four-hour average TRS concentrations above 5 ppm, except that 6 percent of all four-hour averages of TRS concentrations are not considered to be excess emissions if they are less than 10 ppm. The exception does not apply to excess emissions due to malfunctions, startups, or shutdowns of the facility or control device.

(3) For emissions from the digester system, brown stock washer system, multiple-effect evaporator system, black liquor oxidation system, or condensate stripper system where the gases are incinerated in a device other than a recovery furnace or lime kiln: All four-hour average TRS concentrations above 5 ppm, unless the requirements of paragraph (b)(1) of this section are met.

§ 60.285 Test methods and procedures.

(a) Reference methods in Appendix A of this part, except as provided under § 60.8(b), shall be used to determine compliance with § 60.282(a) as follows:

(1) Method 5 for the concentration of particulate matter and the associated moisture content,

(2) Method 1 for sample and velocity traverses,

(3) When determining compliance with § 60.282(a)(2), Method 2 for velocity and volumetric flow rate,

(4) Method 3 for gas analysis, and
(5) Method 9 for visible emissions.

(b) For Method 5, the sampling time for each run shall be at least 60 minutes and the sampling rate shall be at least 0.85 dscm/hr (0.53 dscf/min) except that shorter sampling times, when necessitated by process variables or other factors, may be approved by the Administrator. Water shall be used as the cleanup solvent instead of acetone in the sample recovery procedure outlined in Method 5.

(c) Method 17 (in-stack filtration) may be used as an alternate method for Method 5 for determining compliance with § 60.282(a)(1)(i): *Provided,* That a constant value of 0.009 g/dscm (0.004 gr/dscf) is added to the results of Method 17 and the stack temperature is no greater than 205° C (ca. 400° F). Water shall be used as the cleanup solvent instead of acetone in the sample recovery procedure outlined in Method 17.

(d) For the purpose of determining compliance with § 60.283(a) (1), (2), (3), and (4), the following reference methods shall be used:

(1) Method 16 for the concentration of TRS,
(2) Method 3 for gas analysis, and
(3) When determining compliance with § 60.283(a)(3), Method 2 for velocity and volumetric flow rate.

(e) All concentrations of particulate matter and TRS from the lime kiln and recovery furnace that are measured as required by this section shall be corrected to 10 volume percent oxygen and 8 volume percent oxygen, respectively, when the oxygen concentrations exceed these values.

APPENDIX A—REFERENCE METHODS

2. Method 16 and Method 17 are added to Appendix A as follows:

* * * * *

METHOD 16—SEMICONTINUOUS DETERMINATION OF SULFUR EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability*

1.1 *Principle.* A gas sample is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for gaseous sulfur compounds by gas chromatographic (GC) separation and flame photometric (FPD) detection. Two GC/FPD analytical systems equipped with suitable columns are used for resolution of both low and high molecular weight TRS compounds.

1.2 *Applicability.* This method is applicable for determination of TRS compounds when specified by an applicable subpart.

2. *Range and sensitivity*

2.1 *Range.* The maximum limit of the FPD for each sulfur compound is about 1 ppm. This limit is expanded by dilution of the sample gas before analysis. Kraft mill gas samples are normally diluted tenfold (10:1), resulting in an upper limit of about 10 ppm for each compound.

2.2 *Sensitivity.* The minimum detectable concentration of the FPD is less than 50 ppb.

3. *Interferences*

3.1 *Moisture condensation.* Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

3.2 *Carbon monoxide and carbon dioxide.* CO and CO_2 have a substantial desensitizing effect on the detector even after 10:1 dilution. This potential interference is eliminated by eluting CO and CO_2 with the "air peak" prior to elution of any sulfur compound.

3.3 *Particulate matter.* Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference is eliminated by use of a filtered probe described in Section 5.1.1.

4. *Precision*

4.1 *Calibration precision.* A series of three consecutive injections of the same calibration gas, at any dilution, should produce results which do not vary by more than ±3% from the mean of the three injections.

4.2 *Calibration drift.* The calibration drift determined from the mean of three injections made at the beginning and end of any 8-hour period should not exceed ±3%.

5. *Apparatus*

5.1.1 *Probe.* Figure 16-1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes and the glass wool plugs to reduce clogging of the filter and possible adsorption of sample gas. The exposed portion of the probe between the sampling port and the sample line is heated with heating tape.

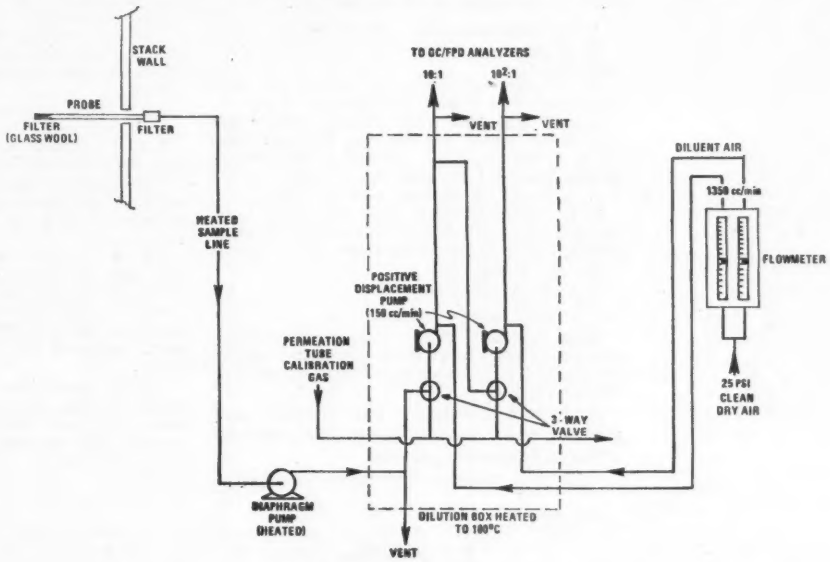

Figure 16-2. Sampling and dilution apparatus.

5.1.2 Sample line—3/16 inch inside diameter Dekoron FEP Teflon[1] tubing, heated to 120° C. This temperature is controlled by a thermostatic heater.

5.1.3 Sample pump—Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120° C by enclosing it in the sample dilution box (5.2.4 below).

5.2 Dilution system—A schematic diagram of the dynamic dilution system is given in Figure 16-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120° C, must be capable of a minimum of 10:1 dilution of sample. Equipment used in the dilution system is listed below:

5.2.1 Dilution pump—Model A-150 Komhyr Teflon positive displacement type, non-adjustable 150 cc/min. ±2.0%, or equivalent, per dilution stage. A 10:1 dilution of sample is accomplished by combining 150 cc of sample with 1350 cc of clean dry air as shown in Figure 16-2.

5.2.2 Valves—Three-way Teflon solenoid or manual type.

[1] Mention of trade names or specific products does not constitute an endorsement by the Environmental Protection Agency.

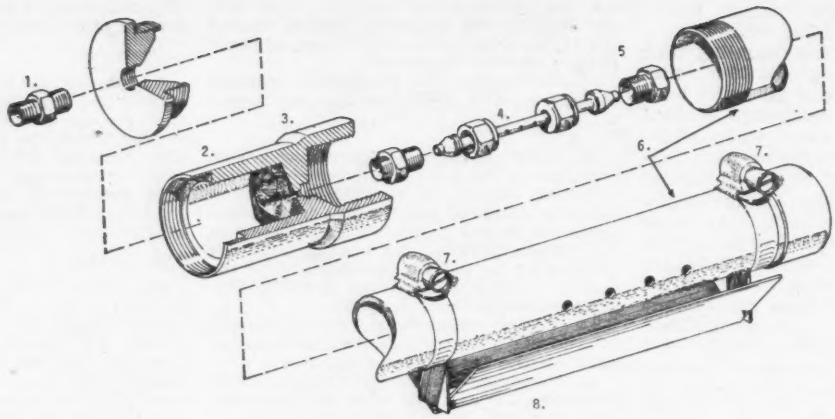

Figure 16-1. Probe used for gas containing high particulate loadings.

DESCRIPTION OF FIGURE 16–1

1. ¼" male connector ⅛" pipe size.
2. A Gelman[1] filter—this filter has glass wool inside.
3. 1" pipe cap which is drilled out and welded on the end of the Gelman filter.
4. ¼" stainless steel tubing with four 1/16" holes drilled all the way through both sides. These holes are ¼" apart. The tubing is also packed with glass wool inside.
5. ¼" cap for capping end of tubing.
6. 1" stainless steel pipe thread at both ends, four ⅛" holes or drilled all the way through both sides. These holes are 1" apart.
7. 1½" clamps.
8. A V-type deflector.
9. 1" pipe cap.

5.2.3 Tubing—Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

5.2.4 Box—Insulated box, heated and maintained at 120° C, of sufficient dimensions to house dilution apparatus.

5.2.5 Flowmeters—Rotameters or equivalent to measure flow from 0 to 1500 ml/min ±1% per dilution stage.

5.3 Gas Chromatograph Columns—Two types of columns are used for separation of low and high molcular weight sulfur compounds:

5.3.1 Low Molecular Weight Sulfur Compounds Column (GC/FPD–1).

5.3.1.1 Separation Column—11 m by 2.16 mm (36 ft by 0.085 in) inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 5% polyphenyl ether and 0.05% orthophosphoric acid, or equivalent (see Figure 16–3).

5.3.1.2 Stripper or Precolumn—0.6 m by 2.16 mm (2 ft by 0.085 in) inside diameter Teflon tubing packed as in 5.3.1.

5.3.1.3 Sample Valve—Teflon ten-port gas sampling valve, equipped with a 10 ml sample loop, actuated by compressed air (Figure 16–3).

5.3.1.4 Oven—For containing sample valve, stripper column and separation columm. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100° C, constant within ±1° C.

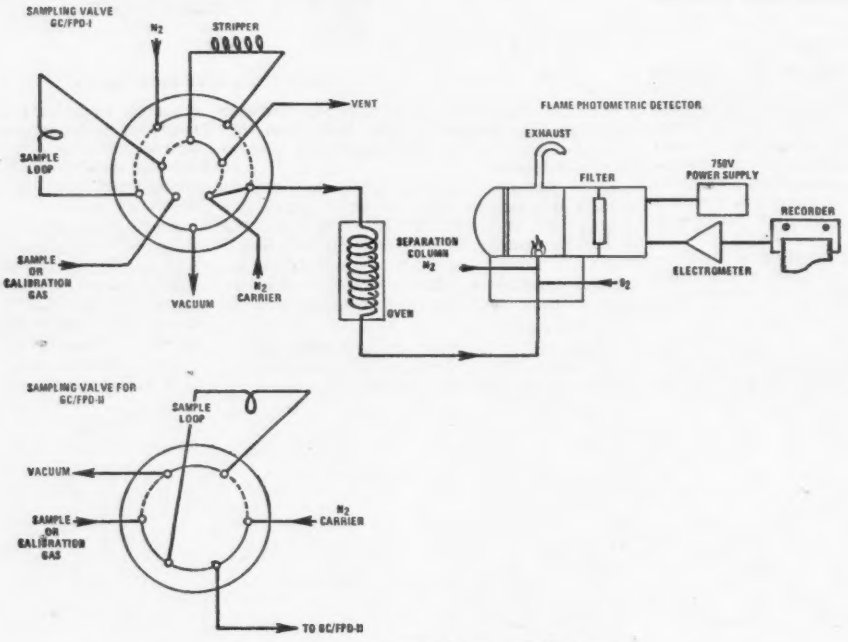

Figure 16-3. Gas chromatographic-flame photometric analyzers.

5.3.1.5 Temperature Monitor—Thermocouple pyrometer to measure column oven, detector, and exhaust temperature ±1° C.

5.3.1.6 Flow System—Gas metering system to measure sample flow, hydrogen flow, oxygen flow and nitrogen carrier gas flow.

5.3.1.7 Detector—Flame photometric detector.

5.3.1.8 Electrometer—Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

5.3.1.9 Power Supply—Capable of delivering up to 750 volts.

5.3.1.10 Recorder—Compatible with the output voltage range of the electrometer.

5.3.2 High Molecular Weight Compounds Column (GC/FPD–II).

5.3.2.1 Separation Column—3.05 m by 2.16 mm (10 ft by 0.085 in.) inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 10 percent Triton X–305, or equivalent.

5.3.2.2 Sample Valve—Teflon six-port gas sampling valve equipped with a 10 ml sample loop, actuated by compressed air (Figure 16–3).

5.3.2.3 Other Components—All components same as in 5.3.1.4 to 5.3.1.10.

5.4 Calibration—Permeation tube system (Figure 16–4).

5.4.1 Tube Chamber—Glass chamber of sufficient dimensions to house permeation tubes.

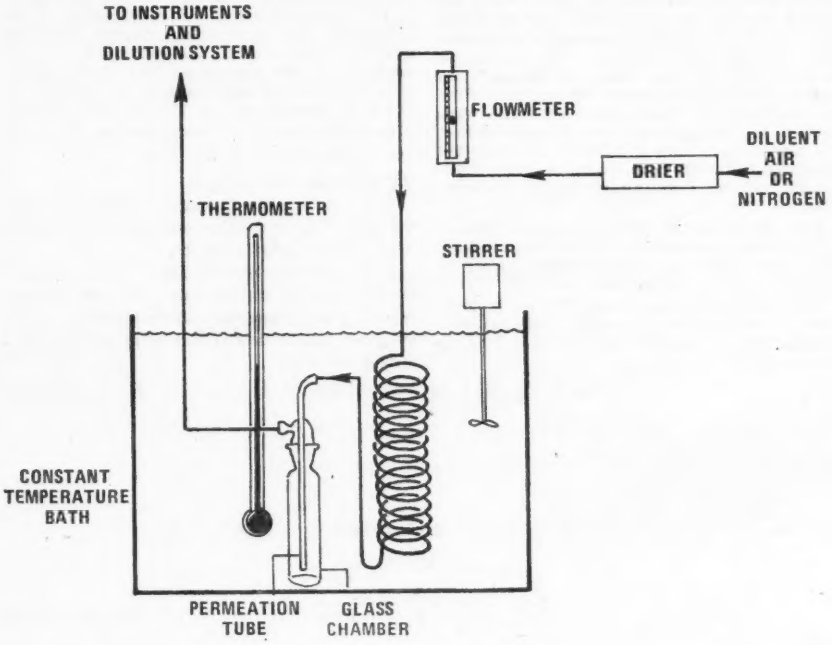

Figure 16-4. Apparatus for field calibration.

5.4.2 Mass Flowmeters—Two mass flowmeters in the range 0–3 l/min. and 0–10 l/min. to measure air flow over permeation tubes at ±2%. These flowmeters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flowmeters, set and monitor the flow rate of gas over the permeation tubes. Injection of calibration gas generated at this flow rate as measured by one flowmeter followed by injection of calibration gas at the same flow rate as measured by the other flowmeter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flowmeter shall be calibrated prior to the first test with a wet test meter and thereafter, at least once each year.

5.4.3 Constant Temperature Bath—Capable of maintaining permeation tubes at certification temperature of 30° C within ±0.1/ C.

5.4.4 Temperature Monitor—Thermometer or equivalent to monitor bath temperature within ±0.1° C.

6. *Reagents*

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) research purity or better.

6.3 Carrier gas. Nitrogen (N_2) prepurified grade or better.

6.4 Diluent. Air containing less than 0.5 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in Section 8.4.

6.5 Compressed Air. 60 psig for GC valve actuation.

6.6 Calibration Gases. Permeation tubes gravimetrically calibrated and certified at 30.0° C.

7. *Pre-test Procedures*

7.1 After the complete measurement system has been set up at the site and verified to be operational, the following procedures shall be completed before sampling is initiated.

7.1.1 Flowmeter Calibration and Leak Test—Appropriate calibration and leak test procedures shall be employed to verify the accuracy and/or integrity of all flowmeters, sample lines, and connections. For components under negative pressure (lines and connections upstream of the sample pump) a leak test is performed using the sample pump to pull a vacuum. Attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 50 mm (2 in.) Hg vacuum. Close off the pump outlet, then stop the pump and ascertain that there is no leak for 5 minutes. For components subject to positive pressure, leak tests shall be performed at each joint by applying a liquid (detergent in water, for example) which will foam in the presence of a leak.

Since the complete dilution system and GC/FPD is calibrated prior to and following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. If any component, or if the complete system fails to respond in a normal and predictable manner, the source of the discrepancy shall be identified and corrected before proceeding.

7.1.2 Mass Flowmeter Calibration—Since all sample calculations are based on the accuracy of air flow measured by the mass flowmeters, it is essential that the cross-calibration check of Section 5.4.2 be followed.

7.1.3 Prior to any sampling run, calibrate the system using the procedures set forth in Section 8. If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in Section 8, after the last run made within the 24-hour period.

8. *Calibration*

8.1 General considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components; particularly the GC/FPD. The references cited at the end of this method are recommended for review for this purpose.

8.2 Permeation Tubes. Under the following procedure, accurately known concentrations (±1%) of a variety of sulfur compounds are generated by passing clean dry air or other diluent gas over permeation tubes, each containing a specific sulfur compound as a permeant. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquefied gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

8.3 Calibration Procedure. Assemble the permeation tube calibration apparatus as depicted in Figure 16–4. Insert the permeation tubes into the glass tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within ±0.1° C. A temperature of 30° C is recommended for the sulfur gas tubes. Allow twenty-four hours for the tubes to equilibrate. When equilibrated, vary the flow rate of diluent air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical

systems. The concentration in parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = K \frac{P_r}{ML}$$

Equation 16–1

where:
C = Concentration of permeant produced in ppm.
P_r = Permeation rate of the tube in μg/min.
M = Molecular weight of the permeant $\left(\frac{g}{g\text{-mole}}\right)$.
L = Flow rate, l/min, of air over permeant @20°C, 760 mm Hg.
K = Gas constant at 20°C and 760 mm Hg = 24.04 l/g mole

8.4 Operating Conditions for GC/FPD Systems.

8.4.1 Low-Molecular Weight Sulfur Compounds—The operating parameters for the GC/FPD system used for low molecular weight compounds are as follows: nitrogen carrier gas flow rate of 50 cc/minute, exhaust temperature of 110° C, detector temperature of 105° C, oven temperature of 40° C, hydrogen flow rate of 80 cc/minute, oxygen flow rate of 20 cc/minute, and sample flow rate between 20 and 80 cc/minute.

8.4.2 High-Molecular Weight Sulfur Compounds—The operating parameters for the GC/FPD system for high molecular weight compounds are the same as in 8.4.1. except: oven temperature of 70° C, and nitrogen carrier gas flow of 100 cc/minute.

8.5 Calibration of GC/FPD Analysis Systems. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.05 to 1.0 ppm) for each sulfur compound anticipated to be present in the gas stream analyzed. Bypassing the dilution system, inject these standards into the GC/FPD analyzers and monitor the responses. Three injects for each concentration must yield the precision described in Section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding. Peak heights, rather than integrated areas, have proven satisfactory; however, integrated areas may be required for alternate columns or instrumentation.

8.5. Calibration Curves—Plot the GC/FPD responses in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound calibrated.

8.6 Calibration of Dilution System. Generate a known concentration of hydrogen sulfide using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted is approximated. Inject the diluted calibration gas into GC/FPD–I and monitor its response. Three injects for each dilution must yield the precision described in Section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration curve for H_2S (developed under 8.4.1) determine the diluted calibration gas concentration in ppm. Then, calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. Repeat this procedure for each stage of dilution required.

9. *Sampling and analysis procedure*

9. Sampling. Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 10:1 using the dilution system shown in Figure 16–2. Note that the precise dilution factor is that which is determined in paragraph 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of diluted sample are injected simultaneously into both GC/FPD analyzers for analysis. GC/FPD–I is used to measure the low-molecular weight reduced sulfur compounds. The low molecular weight compounds include hydrogen sulfide, sulfur dioxide, methyl mercaptan, ethyl mercaptan, and dimethyl sulfide. GC/FPD–II is used to resolve the high-molecular weight compounds. The high molecular weight compounds include propyl mercaptan, butyl mercaptan, dimethyl disulfide, dipropyl sulfide, and dibutyl sulfide.

9.2.1 Analysis of Low-Molecular Weight Sulfur Compounds—The sample valve is actuated for one to three minutes in which time an aliquot of diluted sample is injected into the stripper column and analytical column. The valve is then de-actuated for approximately fifteen minutes in which time, the analytical column continues to be foreflushed, the stripper column is backflushed, and the sample loop is refilled. Monitor the responses. The elution time for each compound will be determined during calibration.

9.2.2 Analysis of High-Molecular Weight Sulfur Compounds—The procedure is essentially the same as above except that no stripper column is needed.

9.2.3 Sample Run—A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.4 Observation for Clogging of Probe—If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the sample probe is clogged with particulate matter. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

10. *Post-Test procedures*

10. Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in Section 8. Only H_2S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.4) and the dilution system (8.5).

10. Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.1. The calibration drift must not exceed the limits set forth in paragraph 4.2. If the drift exceeds this limit, the intervening run or runs shall be considered not valid.

11. *Calculations*

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves.

11.2 Calculation of TRS. Total reduced sulfur will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during a given analysis.

$$\text{TRS} = \Sigma(H_2S, \text{MeSH}, 2\text{DMS}, x)d$$

Equation 16–2

where
TRS = Total reduced sulfur in ppm, wet basis.
H_2S = Hydrogen sulfide, ppm.
MeSH = Methyl mercaptan, ppm.
DMS = Dimethyl sulfide, ppm.
DMDS = Dimethyl disulfide, ppm.
x = Other reduced sulfur compounds.
d = Dilution factor, dimensionless.

11.3 Average TRS. The average TRS will be determined as follows:

$$\text{Avg. TRS} = \frac{\sum_{i}^{N}=1\ TRS_i}{N\ (1-Bwo)}$$

Equation 16–3

where:
Avg. TRS = Average total reduced sulfur in ppm, dry basis.
TRS_i = Total reduced sulfur in ppm as determined by Equation 16–2.
N = Number of analyses performed.
Bwo = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases (36 FR 24887).

12. *Bibliography.*

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12.4 Devonald, R. H., Serenius, R. S., and McIntyre, A. D., "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds," Pulp and Paper Magazine of Canada, 73, 3 (March, 1972).

12.5 Grimley, K. W., Smith, W. S., and Martin, R. M., "The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van," presented at the 63rd Annual APCA Meeting in St. Louis, Mo., June 14–19, 1970.

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METHOD 17—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES (IN-STACK FILTRATION METHOD)

Introduction. Particulate matter is not an absolute quantity; rather it is a variable which is a function of temperature and pressure. For this reason, particulate matter emission regulations and/or associated test methods must define or take cognizance of the temperature and pressure at which particulate matter is to be measured. If temperature is not defined, and if the effect of temperature upon the quantity of particulate in an effluent gas is unknown, then the particulate emission regulation may be variable. The range of pressure which exist from source to source is of negligible importance.

In Method 5, 250° F is established as a nominal reference temperature. Thus, where Method 5 is specified under an applicable subpart, particulate matter is defined with respect to temperature. In order to maintain this indicated temperature, Method 5 includes a heated glass sample probe and a heated filter holder. This equipment is cumbersome and requires care in its operation. Therefore, where particulate matter concentrations (over the normal range of temperature associated with a specified source category) are known to be independent of temperature, it is desirable to eliminate the glass

probe and heating system, and sample at stack temperature.

This method describes an in-stack sampling system and sampling procedures for use where particulate matter concentrations are independent of temperature. It may be used to conduct performance tests under 40 CFR 60.8 within specified conditions, or when approved by the Administrator.

1. Principle and applicability

1.1 Principle. Particulate matter is withdrawn isokinetically from a gas stream and collected on a glass fiber filter maintained at stack temperature. The particulate matter mass is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method applies to the measurement of particulate matter emissions from stationary sources and is used to determine compliance with new source performance standards, when specifically provided for in an applicable subpart of the standards. This method is not applicable when stack gases are saturated with water vapor or when the projected cross-sectional are of the probe extension-filter holder assembly (when inserted halfway into the stack) covers more than 3% of the stack cross-sectional area (see Section 4.1.2).

2. Apparatus

2.1 Sampling train. A schematic of the sampling train used in this method is shown in Figure 17-1. Construction details for many, but not all, of the train components are given in APTD-0581; for changes from the APTD-0581 document and for allowable modifications to Figure 17-1, consult with the Administrator.

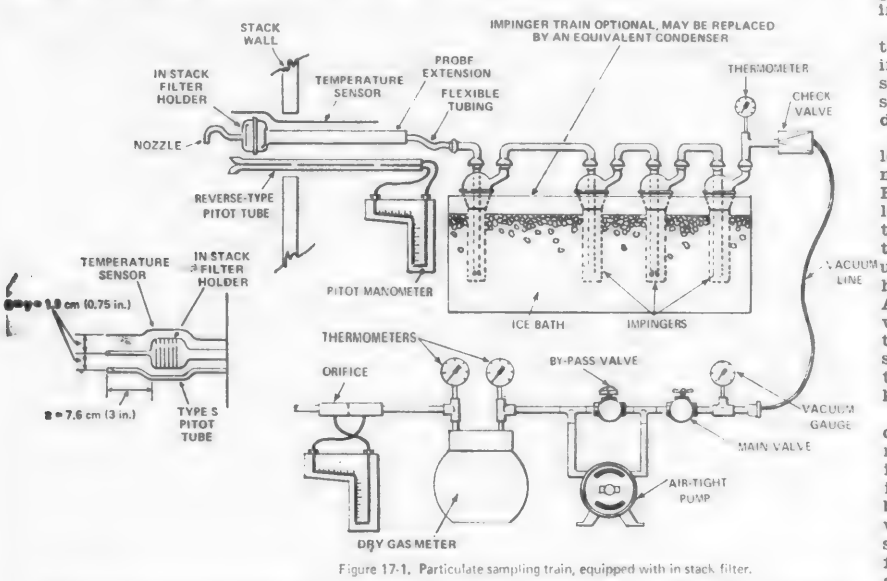

Figure 17-1. Particulate sampling train, equipped with in-stack filter.

The operating and maintenance procedures for many of the sampling train components are described in APTD-0576. Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenace procedures outlined in it, unless otherwise specified herein.

2.1.1 Probe nozzle—Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be ≤30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Administrator. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used subject to approval from the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 cm (⅛ in.) up to 1.27 cm (½ in.) (or larger if higher volume sampling trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (⅛ in.). Each mozzle shall be calibrated according to the procedures outlined in the calibration section.

2.1.2 Filter Holder. The in-stack filter holder shall be constructed of borosilicate or quartz glass or stainless steel; if a gasket is used, it shall be made of silicone rubber, teflon, or stainless steel. Other holder and gasket materials may be used with approval from the Administrator. The filter holder shall be designed to provide a positive seal against leakage from the outside or around the filter.

2.1.3 Probe Extension—Any suitable rigid probe extension may be used after the filter holder. Flexible tubing may also be used between the probe extension and the condenser.

2.1.4 Pitot tube—Type S, or other device approved by the Administrator, attached to probe extension to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other, not necessarily in the same plane, during sampling. The free space between the nozzle and pitot tube (see Figure 17-1) shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the largest sized nozzle shall be used to set the free space. In addition, to minimize aerodynamic interactions between the pitot tube and filter holder, there shall be a distance of at least 3 inches between the center line of the pitot tube impact openings and the leading edge of the filter holder (see Figure 17-1).

The pitot tube must meet the criteria specified in Method 2, and be calibrated separately (i.e., apart from its assembly configuration) according to the procedures outlined in that method for the calibration of isolated Type S pitot tubes.

2.1.5 Differential pressure gauge—Inclined manometer capable of measuring velocity head within 10% of the minimum measured value or ±0.013 mm (0.0005 in.), whichever is greater. Below a differential pressure of 1.3 mm (0.05 in.) water guage, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.1.6 Condenser—Any system that cools the sample gas stream (e.g., impingers connected in series, as in Method 5) and allows measurement of both the water condensed and the moisture leaving the condenser, each to within 1 ml or 1 g. The moisture leaving the condenser can be measured either by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law; or (2) passing the sample gas stream through a silica gel trap with exit gases kept below 20° C (68° F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices.

2.1.7 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications in section 2 of this method are met. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

2.1.8 Barometer—Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.9 Gas density determination equipment—Temperature and pressure gauges and gas analyzer as described in Methods 2 and 3.

2.1.10 Temperature and pressure gauges—If Dalton's law is used, to monitor temperature and pressure at condenser outlet. The temperature gauge shall have an accuracy of 1° C (2° F). The pressure gauge shall be capable of measuring pressure to within 2.5 mm. Hg (0.1 in. Hg). If silica gel is used in the condenser system the temperature and pressure must be measured before the silica gel component.

2.2 Sample recovery.

2.2.1 Probe nozzle brush—Nylon bristles with stainless steel wire handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

2.2.2 Glass wash bottles—Two.

2.2.3 Glass sample storage containers—Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1,000 ml. Screw cap closures shall be teflon rubber-backed liners or of such construction so as to be leak free and prevent chemical attack from the acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Other types of containers must be approved by the Administrator.

2.2.4 Petri dishes—For filter samples; glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated cylinder and/or balance—To measure condensed water to within 1 ml. or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances are suitable for use here and in section 2.3.4.

2.2.6 Plastic storage containers—Air tight containers to store silica gel.

2.2.7 Funnel and rubber policeman—To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.3 Analysis.

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance—To measure to within 0.1 mg.

2.3.4 Balance—To measure to within 0.5 g.

2.3.5 Beakers—250 ml.

2.3.6 Hygrometer—To measure the relative humidity of the laboratory environment.

2.3.7 Temperature gauge—To measure the temperature of the laboratory environment.

3. *Reagents*

3.1 Sampling.

3.1.1 Filters—The in-stack filters shall be glass mats or thimble fiber filters, without organic binders, and shall exhibit at least 99.95% efficiency (≤0.05% penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency tests shall be conducted in accordance with ASTM standard method D 2986–71. Test data from the supplier's quality control program is sufficient for this purpose.

3.1.2 Silica gel—Indicating type, 6–16 mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received.

3.1.3 Crushed ice.

3.1.4 Stopcock grease—Acetone insoluble, heat stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used.

3.2 Sample recovery.

3.2.1 Acetone—Reagent grade, ≤0.001% residue, in glass bottles. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers. Thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤0.001%) shall be used.

3.3 Analysis.

3.3.1 Acetone—Same as 3.2.1.

3.3.2 Desiccant—Anhydrous calcium sulfate, indicating type.

4. *Procedure*

4.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure.

4.1.1 Pretest preparation. All the components shall be maintained and calibrated according to the procedure described in APTD–0576, unless otherwise specified herein.

Weigh approximately 200–300 g of silica gel in air tight containers to the nearest 0.5 g. Record the total weight, both silica gel and container, on each container. Larger portions of silica gel may be used, but care should be taken during sampling that the gel is not entrained and carried out of its holder. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of proper size on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20±5.6° C (68±10° F) and ambient pressure for at least 24 hours and weigh at 6 or more hour intervals to a constant weight, i.e., 0.5 mg change from previous weighing, and record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50%.

4.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Make a projected area model of the probe extension-filter holder assembly, with the pitot tube impact openings positioned along the centerline of the stack, as shown in Figure 17–2. If the estimated cross-section blockage, calculated as shown in Figure 17–2, exceeds 3 percent of the duct cross sectional area, then either one of the following shall be done: (1) a suitable out-stack filtration method can be used instead of in-stack filtration; or (2) a special in-stack assembly, designed to minimize blockage effects, can be used. For details concerning the latter approach, consult with the Administrator.

Determine the stack pressure, temperature, and the range of velocity heads using Method 2; determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

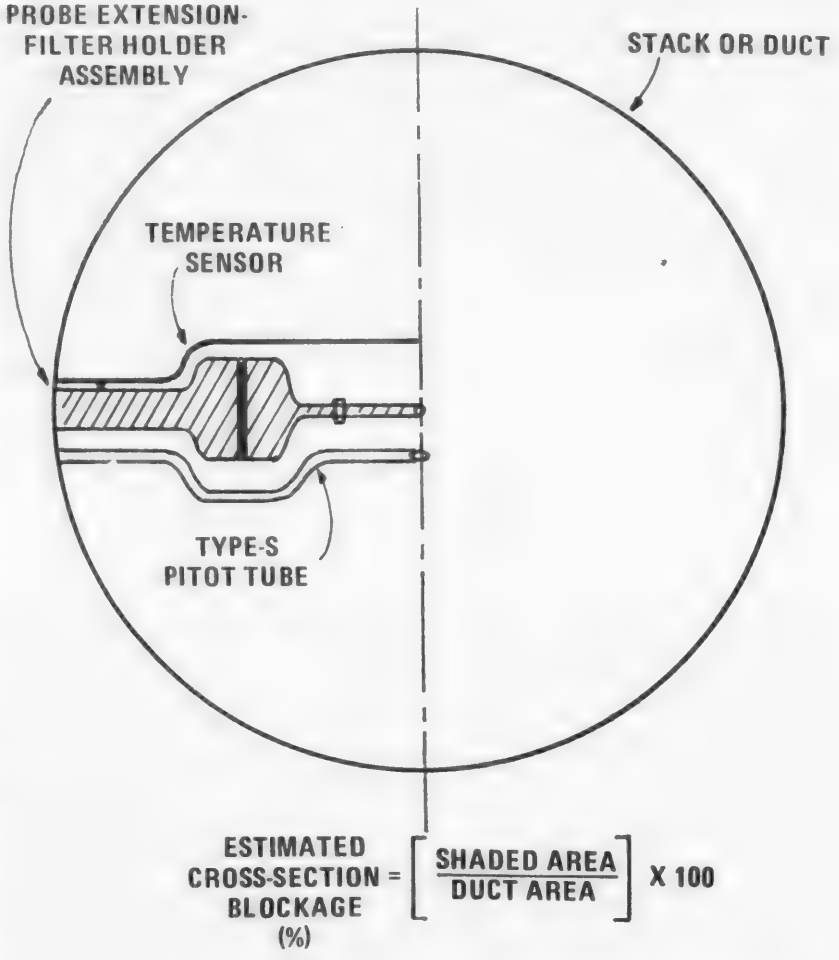

Figure 17-2. Projected-area model of cross-section blockage (approximate average for a sample traverse) caused by in-stack filter holder-probe extension assembly.

Select a nozzle size based on the range of velocity heads such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the differential pressure gauge is capable of measuring the minimum velocity head value to within 10%, or as specified by the Administrator.

Select a probe extension length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that the sampling time per point is not less than 2 min. (or some greater time interval if specified by the Administrator) and the sample volume taken will exceed the required minimum total gas sample volume specified in the test procedures for the specific industry. The latter is based on an approximate average sampling rate. Note also that the minimum total sample volume is corrected to standard conditions.

It is recommended that half-integral or integral numbers of minutes be sampled at each point in order to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of collection train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

If impingers are used to condense stack gas moisture prepare them as follows: place 100 ml of water in each of the first two impingers; leave the third impinger empty; and transfer approximately 200–300 g or more, if necessary, of preweighed silica gel from its container to the fourth impinger; alternatively, if a balance is available in the field, the silica gel can be weighed out in a tared impinger, and its weight gain determined in the field. Place the silica gel container in a clean place for later use in the sample recovery. If some means other than impingers is used to condense moisture, prepare the condenser (and, if appropriate, silica gel for condenser outlet) for use.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as not to allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed. Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Unless otherwise specified by the Administrator, attach a temperature sensor to the probe extension so that the sensor extends beyond the leading edge of the probe extension and does not touch any metal. The sensor should be positioned at least 1.9 cm (0.75 in.) from both the pitot tube and probe nozzle to avoid interference with the gas flow (see Figure 17–1).

Assemble the train as in Figure 17–1, using (if applicable) a very light coat of silicone grease on all ground glass joints and greasing only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease. Place crushed ice around the impingers (if applicable).

4.1.4 Leak check procedure—After the sampling train has been assembled, a leak check of the filter holder shall be conducted as follows: Plug the inlet to the probe nozzle with a material that will be able to withstand the stack temperature; alternatively, the probe nozzle can be removed and the inlet to the filter holder plugged. Insert the holder into the stack and wait approximately 5 minutes (or longer, if necessary) to allow the system to come to equilibrium with the temperature of the stack gas stream. Turn on the pump and draw a vacuum of at least 380 mm Hg (15 in. Hg). Determine the leakage rate, if any. A leakage rate in excess of 4% of the average sampling rate or 0.00057 m³/min. (0.02 cfm), whichever is less, is unacceptable.

The following leak check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until 380 mm Hg (15 in. Hg) vacuum is reached. Do not reverse direction of by-pass valve. If 380 mm Hg (15 in. Hg) is exceeded, either leak check at this higher vacuum or end the leak check as shown below and start over.

When the leak check is completed, first slowly remove the plug from the inlet to the probe nozzle and immediately turn off the vacuum pump. This prevents the water in the condenser from being forced backward and keeps silica gel from being entrained backward.

Leak checks shall be conducted as described whenever the train is disengaged, e.g., for silica gel or filter changes during the test, prior to each test run, and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes at the highest vacuum reading drawn during that sampling traverse.

PLANT _____
LOCATION _____
OPERATOR _____
DATE _____
RUN NO. _____
SAMPLE BOX NO. _____
METER BOX NO. _____
METER $\Delta H@$ _____
C FACTOR _____
PITOT TUBE COEFFICIENT, C_p _____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
ASSUMED MOISTURE, % _____
PROBE EXTENSION LENGTH, m (ft) _____
NOZZLE IDENTIFICATION NO. _____
AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____
LEAK RATE, m³/min (cfm) _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE mm Hg (in Hg)	STACK TEMPERATURE (T_s) °C (°F)	VELOCITY HEAD (ΔP_s), mm H₂O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H₂O (in H₂O)	GAS SAMPLE VOLUME m³ (ft³)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)	
TOTAL							Avg.	Avg.	
AVERAGE							Avg.		

Figure 17-3. Particulate field data.

4.1.5 Particulate train operation—During the sampling run, maintain the isokinetic sampling rate to within 10% (unless otherwise specified by the Administrator) of true isokinetic.

For each run, record the data required on the example data sheet shown in Figure 17–3. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available for use whenever the Type S pitot tube coefficient is 0.85±0.02, and the stack gas equivalent density (molecular weight) is 29±4. APTD–0576 details the procedure for using these nomographs. If C_p and M_s are outside the above stated ranges, do not use the nomograph unless appropriate steps (see Reference 7.7) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes, to minimize chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain a temperature of less than 20° C (68° F) at the condenser outlet; this will prevent excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes to high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter holder-nozzle assembly be used rather than attempting to change the filter itself. After the new filter holder-nozzle assembly is installed, conduct a leak check. The particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except for filter and silica gel changes. However, if approved by the Administrator, two or more trains may be used for a single test run when there are two or more ducts or sampling ports. The results shall be the total of all sampling train catches.

At the end of the sample run, turn off the pump, remove the probe extension-filter holder-nozzle assembly from the stack, and record the final dry gas meter reading. Perform a leak check at a vacuum equal to or greater than the maximum reach during sampling. Calculate percent isokinetic (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Adminstrator for possible variance on the isokinetic rates.

4.2 Sample recovery. Proper cleanup procedure begins as soon as the probe extension-filter holder-nozzle assembly is removed from the stack at the end of the sampling period. Allow the assembly to cool.

When the assembly can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, and force condenser water backward.

Before moving the sample train to the cleanup site, disconnect the filter holder-probe nozzle assembly from the probe extension; cap the open inlet of the probe extension. Be careful not to lose any condensate, if present. Remove the umbilical cord from the condenser outlet and cap the outlet. If a flexible line is used between the first impinger or condenser and the probe extension, disconnect the line at the probe extension and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease (if applicable) cap off the condenser inlet. Ground glass stoppers, plastic caps, or serum caps (whichever are appropriate) may be used to close these openings.

Transfer both the filter holder-probe nozzle and condenser assemblies to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Place about 200 ml of this acetone taken directly from the wash bottle being used in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Quantitatively remove any particulate matter and/or filter which adheres to the filter holder gasket by carefully using a dry nylon bristle brush and/or a sharp-edged blade and place into this container. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe nozzle or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, fitting, and front half of the filter holder by washing these components with acetone and placing the wash into a glass container in the following manner; note that distilled water may be used instead of acetone when approved by the Administrator or shall be used when specified by the Administrator; in these cases, save a water blank and follow Administrator's directions on analysis;

Carefully remove the proble nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse with acetone the inside parts of the fitting in a similar way until no visible particles remain. A funnel may be used to aid in transferring liquid washes to the container. Rinse the brush with acetone and quantitatively collect these washings in the sample container. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints are wiped clean of silicone grease (if applicable), clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter are collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label container to clearly identify its contents.

Container No. 3. Note color of indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel back to its original container and seal. A funnel may make it easier to pour the silica gel without spilling, and a rubber policeman may be used as an aid in removing the silica gel. It is not necessary to remove the small amount of dust particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure under "Analysis."

Condenser water. Treat the condenser or impinger water as follows: make a notation of any color or film in the liquid catch. Measure the condensate to within ±1 ml by using a graduated cylinder or, if available, to within ±0.5 g by using a balance. Record the condensate volume or weight. This information is required to calculate the moisture content of the effluent gas. Discard the liquid after measuring and recording the volume or weight.

4.3 Analysis. Record the data required on the example sheet shown in Figure 17-4. Handle each sample container as follows:

Container No. 1. Leave in shipping container or transfer the filter and any loose particulate from the sample container to a

tared glass weighing dish and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weight to a constant weight and report the results to the nearest 0.1 mg. For purposes of this section 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1% of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings and no more than 2 minutes exposure to the laboratory atmosphere (must be less than 50% relative humidity) during weighing.

Plant _____

Date _____

Run No. _____

Relative Humidity _____

Amount liquid lost during transport _____

Acetone blank volume, ml _____

Acetone wash volume, ml _____

Acetone blank concentration, mg/g (equation 17-4) _____

Acetone wash blank, mg (equation 17-5) _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
		Less acetone blank	
		Weight of particulate matter	

	VOLUME OF LIQUID WATER COLLECTED		
	CONDENSATE VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g	ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml)

$$\frac{\text{INCREASE, g}}{\text{1 g/ml}} = \text{VOLUME WATER, ml}$$

Figure 17-4. Analytical data.

Container No. 2. Note level of liquid in container and confirm on analysis sheet whether or not leakage occurred during transport. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel to the nearest 0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

5. *Calibration*

Maintain a laboratory log of all calibrations.

5.1 Probe nozzle. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make 3 separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

5.2 Pitot tube. The pitot tube shall be calibrated separately (i.e., apart from its assembly configuration) according to the procedures outlined in Method 2 for Calibration of Isolated Type S pitot tubes.

5.3 Dry gas meter and orifice meter. Both meters shall be calibrated according to the procedure outlined in APTD–0576. When a diaphragm pump is used, assure that there is no leak.

5.4 Temperature gauges. Calibrate dial and liquid filled bulb thermometers and thermocouple-potentiometer systems against mercury-in-glass thermometers. Ice bath and boiling water (corrected for barometric pressure) are acceptable reference points. For other devices, check with the Administrator.

6. *Calculations*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature.

A_n = Cross sectional area of nozzle, m² (ft²).
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_a = Acetone blank residue concentration, mg/g.
c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g dscf).
I = Percent of isokinetic sampling.
m_n = Total amount of particulate matter collected, mg.
M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole).
m_a = Mass of residue of acetone after evaporation, mg.
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
P_s = Absolute stack gas pressure, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R = Ideal gas constant, 0.06236 mm Hg-m³/°K-g-mole (21.83 in. Hg-ft³/°R-lb-mole).
T_m = Absolute average dry gas meter temperature (see Figure 17-3), °K (°R).
T_s = Absolute average stack gas temperature (see Figure 17-3), °K (°R).
T_{std} = Standard absolute temperature, 293° K (528° R).
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash, ml.
V_{lc} = Total volume of liquid collected in condenser and silica gel (see Figure 17-4), ml.
V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).
$V_{w(std)}$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).
v_s = Stack gas velocity, calculated by Method 2, Equation 2-7 using data obtained from Method 17, m/sec (ft/sec).
W_a = Weight of residue in acetone wash, mg.
ΔH = Average pressure differential across the orifice meter (see Figure 17-3), mm H_2O (in. H_2O).
ρ_a = Density of acetone, mg/ml (see label on bottle).
ρ_w = Density of water, 1 g/ml (0.00220 lb/ml).
θ = Total sampling time, min.
13.6 = Specific gravity of mercury.
60 = sec/min.
100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 17-3).

6.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 17-1.

$$V_{m(std)} = V_m \left(\frac{T_{std}}{T_m}\right)\left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}\right] = KV_m\left[\frac{P_{bar} + \Delta H/13.6}{T_m}\right] \qquad \text{Equation 17-1}$$

where:
K = 0.3855 °K/mm Hg for metric units
= 17.65 °R/in. Hg for English units

6.4 Volume of water vapor.

$$V_{w(std)} = V_{lc}\left(\frac{\rho_w}{M_w}\right)\left(\frac{RT_{std}}{P_{std}}\right) = KV_{lc} \qquad \text{Equation 17-2}$$

where
K = 0.00134 m³/ml for metric units
= 0.0472 ft³/ml for English units

6.5 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Equation 17-3}$$

6.6 Acetone blank concentration.

$$C_a = \frac{m_a}{V_a \rho_a} \qquad \text{Equation 17-4}$$

6.7 Acetone wash blank.

$$W_a = C_a V_{aw} \rho_a \qquad \text{Equation 17-5}$$

6.8 Total particulate weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 17-4).

6.9 Particulate concentration.

$$c_s = (0.001 \text{ g/mg})\ (m_n/V_{m(std)}) \qquad \text{Equation 17-6}$$

6.10 Conversion factors:

From	To	Multiply by
scf	m^3	0.0283
g/ft^3	gr/ft^3	15.4
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

6.11 Isokinetic variation.

6.11.1 Calculations from raw data.

$$= \frac{100\ T_s[KV_{lc} + (V_m/T_m)(P_{bar} + \Delta H/13.6)]}{60\ \theta v_s P_s A_n} \qquad \text{Equation 17-7}$$

where:
K = 0.00346 mm Hg-m^3/ml-°K for metric units
= 0.00267 in. Hg-ft^3/ml-°R for English units

6.11.2 Calculations from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std}\ 100}{T_{std} v_s \theta A_n P_s\ 60\ (1 - B_{ws})} = K \frac{T_s V_{m(std)}}{P_s v_s A_n \theta (1 - B_{ws})} \qquad \text{Equation 17-8}$$

where:
K = 4.323 for metric units
= 0.0944 for English units

6.12 (Acceptable results. If $90\% \leq I \leq 110\%$, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results. Use reference 7.4 to make judgments. Otherwise, reject the results and repeat the test.

7. References

7.1 Addendum to Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, Dec. 6, 1967.

7.2 Martin, Robert M., Construction Details of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0581.

7.3 Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0576.

7.4 Smith, W. S., R. T. Shigehara, and W. F. Todd, A Method of Interpreting Stack Sampling Data, Paper presented at the 63rd Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14–19, 1970.

7.5 Smith, W. S., et al., Stack Gas Sampling Improved and Simplified with New Equipment APCA paper No. 67–119, 1967.

7.6 Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.

7.7 Shigehara, R. T., Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights, Stack Sampling News 2:4–11, Oct. 1974.

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ENVIRONMENTAL PROTECTION AGENCY

[FRL 605–1]

AIR POLLUTION PREVENTION AND CONTROL

Notice of Addition to the List of Categories of Stationary Sources

Section 111 of the Clean Air Act (42 U.S.C. 1857c–6) directs the Administrator of the Environmental Protection Agency to publish, and from time to time revise, a list of categories of stationary sources which he determines may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare. Within 120 days after the inclusion of a category of stationary sources in such list, the Administrator is required to propose regulations establishing standards of performance for new and modified sources within such category. At present standards of performance for twenty-four categories of sources have been promulgated.

The Administrator, after evaluating available information, has determined that kraft pulp mills are an additional category of stationary sources which meets the above requirements. The basis for this determination is discussed in the preamble to the proposed regulation that is published elsewhere in (Part II) this issue of the FEDERAL REGISTER. Evaluation of other stationary source categories is in progress, and the list will be revised from time to time as the Administrator deems appropriate. Accordingly, notice is given that the Administrator, pursuant to section 111(b)(1)(A) of the Act and after consultation with appropriate advisory committees, experts, and Federal departments and agencies in accordance with section 117(f) of the Act, effective (date of publication) amends the list of categories of stationary sources to read as follows:

LIST OF CATEGORIES OF STATIONARY SOURCES AND CORRESPONDING AFFECTED FACILITIES

* * * * *

Source Category

25. Kraft pulp mills.

* * * * *

Affected Facilities

- Digester System.
- Brown Stock Washer System.
- Multiple Effect Evaporator System.
- Black Liquor Oxidation System.
- Recovery Furnace.
- Smelt Dissolving Tank
- Lime Kiln.
- Condensate Stripper System.

Proposed standards of performance applicable to the above source category appear elsewhere in Part II this issue of the FEDERAL REGISTER.

Dated: September 16, 1976.

JOHN QUARLES,
Acting Administrator.

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